AN IMPROVED HYDROGEN ELECTRODE

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XVIII. AN IMPROVED HYDROGEN ELECTRODE.

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Further use of hydrogen electrode vessels of the type described [Walpole, 1913] has resulted in some modifications justified by the more accurate results obtained.

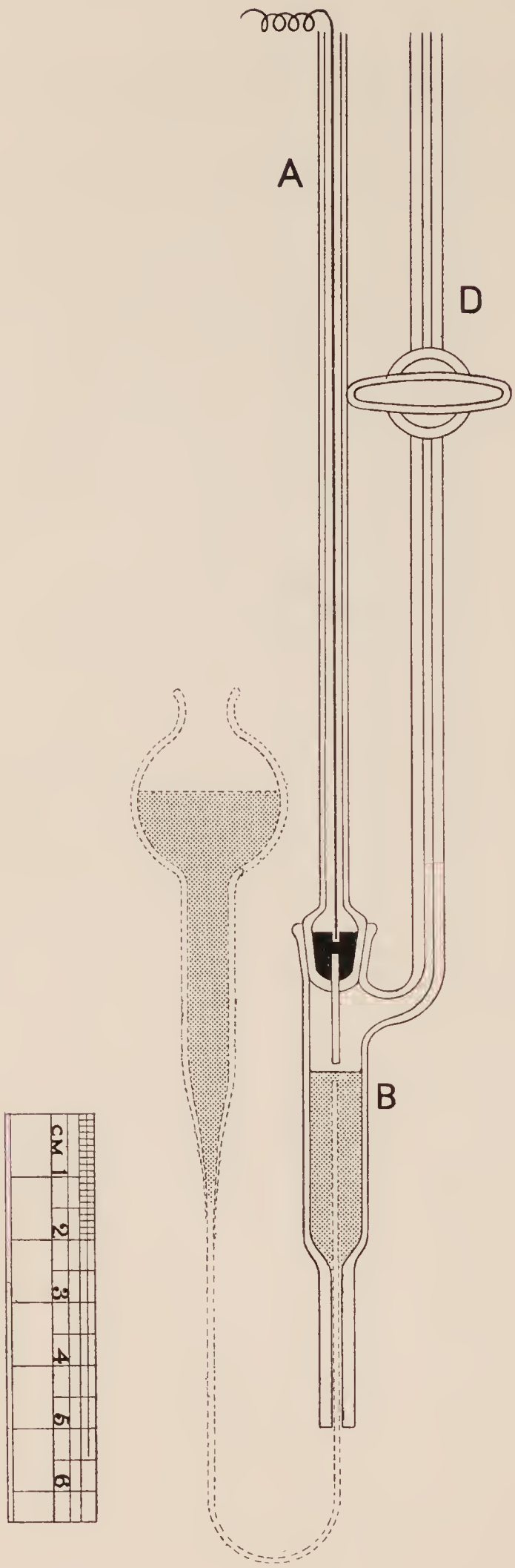
In the actual construction of the vessel the rubber stopper sometimes employed [1913, p. 411] was finally discarded, and a ground glass joint used instead where the glass tube *A*, carrying the electrode, fits into the outer tube *B*.

Both the electrode vessel, and the pipette necessary for refilling it when the fluid under investigation contains carbon dioxide, are made of hardest Jena glass, e.g. *Borosilicate glass, Jena* 59. 111. The slow rise of E.M.F. due to liberation of alkali from the glass is thereby avoided. The general dimensions are those given [1913, p. 415]. The description of a smaller electrode for electrometric titration [1913, p. 418] contains an error. Its capacity was 0·3 cc. not 3 cc. as stated.

In describing a determination it is assumed that the vessel is wet with the last fluid examined. Starting with a clean dry vessel the volume of fluid required is, naturally, smaller. The hydrogen supply is connected to *D*, and the air displaced. The tap on the T-piece [1913, p. 419] is shut, and, by means of the filling syringe, some of the liquid examined is drawn up into *B* and used to rinse it out. To do this *D* is shut and the electrode vessel tilted about the horizontal position.

For very careful work it is well to undo the ground glass joint and wet the surfaces with the experimental fluid before starting.

After emptying out the rinsing fluid by opening *D* and pushing home the piston of the filling apparatus, hydrogen is passed again for a second or two and the lower end of *B* dipped below the experimental fluid. The actual sample employed for the determination is then drawn up until the meniscus is just touching the blacked platinum point and the tap *D* is


A
D
B
CM
1
2
3
4
5
6

closed. The rubber tube from the filling apparatus may now be detached. If the fluid contains no carbon dioxide the electrode vessel is placed at once in the trough containing saturated potassium chloride at 18°.

If carbon dioxide is present the hydrogen bubble must be passed backwards and forwards (five minutes is sufficient) till equilibrium is established, and the liquid then replaced by a fresh sample of experimental fluid from the pipette. To do this, the pipette, filled with the solution, is brought into the position shown in the diagram and in a short while the contents of *B* will be replaced. The hydrogen bubble is again passed to and fro for five minutes and the fluid replaced again. Three replacements are sufficient.

The size of the bubble will be found now to have increased. Connection to the filling apparatus and gentle suction with the lower end of the electrode vessel immersed in experimental fluid enables the adjustment of the meniscus to the platinum point to be made accurately. The electrode vessel is now placed in the potassium chloride trough without delay.

The pipette has a capacity of about 4 cc. and is half filled for each replacement. There is no need for a stopper of any kind at the bottom of the electrode vessel as capillary forces are quite sufficient to prevent egress of fluid or intake of air during manipulation. In those cases where blood-protein and similar solutions are examined the lowered surface tension produces difficulties which may be overcome by dipping the lower end of the filled electrode vessel in distilled water for a moment.

A P_H^+ determination of a carbon dioxide-sodium carbonate mixture containing 0·02 N NaCl, made by mixing 20 cc. 0·1 N HCl and 25 cc. 0·1 N Na_2CO_3 and diluting to 100 cc., with water gave the following results:

Time	E.M.F. reading against sat. KCl calomel electrode	
12.4	(Vessel introduced into KCl)	
12.5	0·6100	
12.10	0·6100	
12.30	0·6100	
2.10	0·6100	$P_H^+ = 6·22$

The experiment was commenced with the apparatus wet from a previous determination on another fluid; volume of fluid taken for examination 10 cc.

REFERENCE.

Walpole (1913), *Biochem. J.* **7**, 410.